

Molecular Simulation of Membrane Based Separations of Ethanolic Electrolyte Solutions

H. Yan and S. Murad

Department of Chemical Engineering

University of Illinois at Chicago

Chicago, IL 60607, USA

and

E. Enciso

Department de Quimica Fisica

Universidad Complutense

28040 Madrid, Spain

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ABSTRACT

The method of molecular dynamics has been used to study osmosis, reverse osmosis and electro-osmosis in ethanolic electrolyte solutions. Our results have shown the significant role solvation forces play in reverse osmosis based separations in a wide range of polar solvents. For instance in NaBr solutions, Na^+ ions, despite their rather small molecular size, are prevented from permeating the semi-permeable membrane while ethanol molecules could readily permeate the membrane. This is because of the solvation of the Na^+ ions by the polar solvent and the rather high energy of desolvation (estimated at about 400 kJ/mol, compared to the hydrogen bond energy of ethanol of about 20 kJ/mol) makes the solvated ion rather stable. This in effect increases the apparent size of the Na^+ ions considerably. In fact, it appears that such solvation and possibly adsorption effects do not even permit the Na^+ ions to get close to the membrane walls. In the past it was thought that ions are prevented from crossing the membrane due to surface interactions between the ions and the membrane surface, which were not clearly defined or understood. In our studies there were only Lennard-Jones interactions between the ions and the membrane. We have also found the rate of osmosis and reverse osmosis seems to be significantly effected by the selective adsorption of the various solution components on the membrane.

1. INTRODUCTION

Osmosis, reverse osmosis, and electro-osmosis are all industrially important membrane-based separations processes that involve the separation of gaseous and liquid mixtures. In this paper we report computer simulation studies using a recently developed technique to model semi-permeable membranes realistically, based on an extension of the

NVE molecular dynamics method [1]. The most important feature of our atomistic model is that it permits the permeability as well as the geometry of the membrane to be controlled directly via its molecular parameters. In addition the atoms or molecules that constitute the semi-permeable membrane are also allowed to vibrate or "wobble", as has been found to be essential for realistic simulations of zeolites in several recent studies [2].

Reverse osmosis is a rather energy efficient technique for separating liquid solutions and gas mixtures, with applications amongst others in water purification, treatment of chemical and radioactive wastes as well as in food processing [3-4]. Electro-osmosis, which we define here as the effect of an external electric field on a system undergoing osmosis or reverse osmosis [5], has applications in processes as diverse as desalination of contaminated soils to transdermal drug delivery systems. In a recent previous study [5], we showed that electro-osmosis also has important implications in non-ionic solutions, where it was previously thought not to be important [6]. The overall objective of this study is to understand at the molecular level the phenomena of membrane-separations, and especially to understand which molecular forces (e.g. steric, coulombic etc., play a crucial role in such separations.

2. METHOD

Our simulation method for studying osmosis has been described in detail previously [7-9] so we will only summarize it here. The molecules that constitute the membrane wall are tethered to their equilibrium position by a simple harmonic potential. The structure of the simplest membrane that can be modeled using this technique and the simulation system are

shown in Figure 1. Most simulations were based on a nominal system of 512 particles in the basic cyclically repeated parallelepiped, initially in an fcc configuration, with $L_x=2L_y=2L_z$. L_x was made larger than L_y and L_z to increase the distance between the planes of the two semi-permeable membranes. In this simplest implementation of this method, all molecules with $x=L_x/4$ and $3L_x/4$ in the initial fcc configuration are designated as the pore-wall molecules. We have also done a limited number of simulations with membranes more than one molecule thick, and with membrane structures modeled as thin zeolite films and the results are qualitatively similar. The wall molecules are tethered to their fcc sites as described above with a spring constant of 100 in reduced units using bromide parameters shown later in Table 1. This leads to 64 molecules constituting the two semi-permeable membranes. In the solution compartment (which consists of 224 molecules in total), N_B molecules are designated as solute, equally divided between anions and cations in our studies. The remaining $(224-N_B)$ particles then constitute the solvent molecules of the solution. N_B is fixed to correspond to the desired initial concentration of the solution being investigated, while the size of the simulation cell is fixed to correspond to the initial density of the solution. In the pure solvent compartment (see Figure 1), since the size of the compartment is already fixed, we fix the initial number of solvent molecules N_S to correspond to the desired initial density.

In our investigations we have studied solutions of sodium bromide in ethanol. For ethanol we used the OPLS model (which also accounts for internal rotations in the ethanol molecules) suggested by Jorgensen[10], while for the ions we used the so-called primitive

Semipermeable Membranes

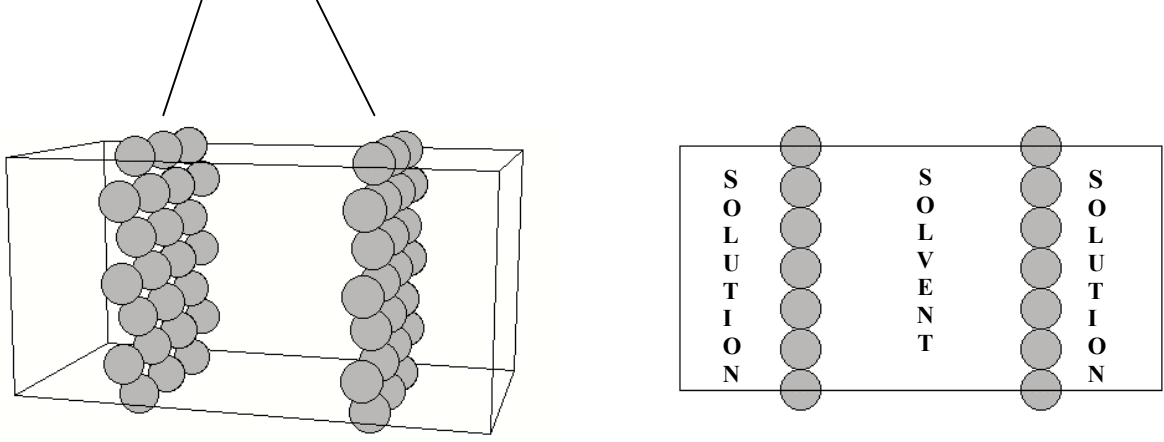


Figure 1. The basic simulation system for osmosis, reverse osmosis and electro-osmosis studies.

model [11]. These models are known to provide a realistic picture of these systems for a wide range of properties [10-11] and are of the form (for interaction between a molecule i and molecule j)

$$u_{ij} = \sum_{\alpha} \sum_{\beta} 4\epsilon_{\alpha\beta} [(\sigma_{\alpha\beta}/r_{\alpha\beta})^{12} - (\sigma_{\alpha\beta}/r_{\alpha\beta})^6] - q_{\alpha}q_{\beta}/r_{\alpha\beta} \quad (1)$$

where the interactions are summed over all active sites α in molecule i and β in molecule j . $r_{\alpha\beta}$ is the scalar distance between the sites α and β , q_{α} and q_{β} the point charges on these sites, while $\epsilon_{\alpha\beta}$ and $\sigma_{\alpha\beta}$ are the energy and size parameters for the interaction between the sites. The intermolecular parameters for eqn. (1) used in our simulations are given in Table

1. The molecules that constitute the membrane were modeled as LJ particles with $\epsilon_{\text{wall}}/\epsilon_{\text{Na}}=0.15$ and σ_{wall} adjusted so that the resulting pores in the wall had a mean diameter of about 5 Å . For cross interactions the OPLS geometric mixing rules were used [10]. All interactions were truncated at 12.5 Å, and long range interactions were modeled using the reaction field method [12-13]. The simulations were carried out at temperatures between 223K and 350K. The pressures (initial) of the solutions studied roughly corresponded to between 1-300 bars. The initial pressure in the solvent compartment was fixed at 1 bar as is usually the case in experimental studies. The simulation consisted of 100,000 equilibration steps, followed by a production run of at least 500,000 time steps of size between 1.08×10^{-15} seconds. This smaller than usual step size was necessary due to the rapid vibrations of molecules in the membrane in our model. In most systems studied these runs were long enough for the system to effectively reach its final equilibrium state. Results reported have been reduced using Br parameters.

Table 1: Intermolecular Parameters for Equation (1)

	$\sigma (\text{\AA})$	$\epsilon (kJ/mol)$	$q (e)$
CH ₃ -	3.905	0.732	0.000
CH ₂ -	3.905	0.494	+ 0.265
-O-	3.070	0.711	- 0.700
-H	0.000	0.700	+ 0.435
Br ⁻	4.730	0.270	- 1.000
Na ⁺	1.900	6.690	+ 1.000

Internal rotations for ethanol were accounted for using a Fourier expansion to represent the rotational potential, $V(\phi)$ for the C-O bond in ethanol.

$$V(\phi) = V_0 + (1/2) V_1(1 + \cos\phi) + (1/2) V_2 (1 - \cos 2\phi) + (1/3) V_3 (1 + \cos 3\phi) \quad (2).$$

The parameters V_i in eqn. (2) are given in [10]. A procedure commonly referred to as "SHAKE" [14-15] was used to solve the equations of motion. The SHAKE algorithm is rather efficient for systems of chain molecules with rotational degrees of freedom. Its essential feature is that at each step of the MD run the constraints (bond length, bond angle, etc) are satisfied exactly [14]. Complete details of this procedure are given elsewhere so we will omit them in this paper. We confirmed the accuracy of our algorithm by comparing our results for pure ethanol systems with those obtained previously by Saiz et al. [16] and Gonzalez et al. [17]. These studies also showed that the potential models for ethanol are adequate for a wide range of properties and state conditions.

3. RESULTS AND DISCUSSION

We have carried out simulations in which the solution compartment contained between 4 and 12 ions, equally divided, of course, between anions and cations. This corresponds roughly to a molar concentration of the electrolyte of between 0.15 – 0.45 M, or a mole fraction of up to 3 percent. Densities are available for electrolyte solutions at normal pressures and these were used to fix the initial densities in our simulations. Densities under pressure were approximated using data on isothermal compressibility [18].

The most important observation from our simulations was that ions were unable to permeate the membrane. This is despite the fact that the ionic diameters (certainly for the

cations) are significantly smaller than those for ethanol, as well as the pore size (see Table 1 and Figure 2). The only exception to this observation was either at high temperatures, or

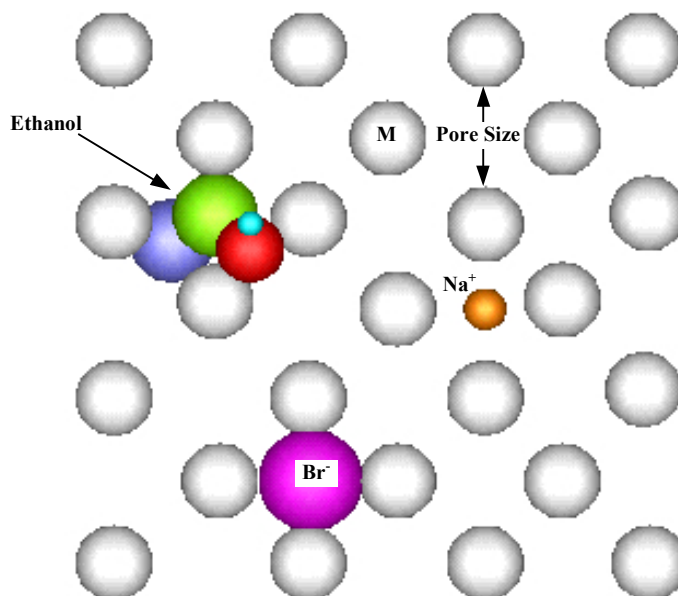


Figure 2: A schematic of the relative sizes of the pore, the solvent and solute in the simulation system. M shows the position and size of the membrane molecules

in the presence of high external electric field, which will be discussed separately, later in this section. In contrast ethanol molecules seemed to be able to permeate the wall rather effortlessly. We have reported similar observations in our previous studies on aqueous and methanolic electrolyte solutions as well [9]. In the past it was thought that the ions are prevented from permeating the membrane, because of interactions between the membrane surface and the ions that are not clearly understood [19-20]. It should be noted that in our intermolecular force model, the membrane molecules are simply treated as LJ particles, with no charges, so that there is no possibility of any unusual interactions between the

membrane and the ions. Despite this, the ions were prevented from crossing the membranes. We believe this is because of the formation of large molecular clusters involving these ions.

We have found evidence, by looking at the molecular configurations in a simulation, of such stable clusters. Most consist of a single ion surrounded by ethanol molecules such as one shown in Figure 3. Other clusters, which are larger and contain two

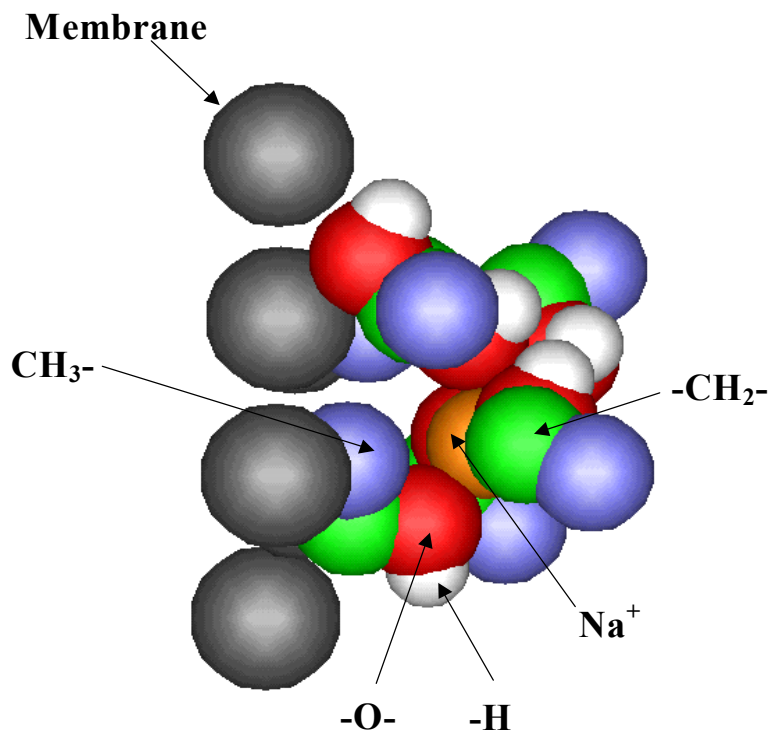


Figure 3: A typical cluster of an ion (Na^+) surrounded by ethanol molecules observed in the simulation. The figure shows how the ions are kept away from the membrane walls by the surrounding ethanol molecules.

or more ions and ethanol molecules, are also likely to be formed, but because of the low concentration of the solution they are less likely in these solutions. In our previous studies we found clusters involving aqueous solutions that did contain more than one ion [21]. These cluster types appear to be stable enough that they do not allow any ions to break away from the cluster and cross the membrane wall. This is understandable, since the enthalpy of solvation of the ions is estimated at 400 kJ/mol, compared to the hydrogen bonding energy of only 20 kJ/mol [22]. The ethanol molecules also form clusters; these clusters however, do not appear to be as stable, so that near the wall, one ethanol molecule can break away from the cluster and cross the membrane quite easily, it appears. This is also shown quite clearly in Figure 4, which shows the density profiles for both ethanol and the ions for a 0.45 M NaBr solution at a temperature of 298 K, and an initial solution pressure of 300 bars. The two membranes separating the solution and solvent compartments are at x/L_x (L_x is the size of the simulation system perpendicular to the membranes) values of 0.25 and 0.75. It can be seen that no ions are present in the solvent compartment at 298 K. From the first adsorption peak of the ions and ethanol, it is also evident that at 298 K the ions are being kept further away from the wall than the ethanol molecules, because of the ethanol molecules associated with the ionic clusters.

The first adsorption peak of ethanol is quite significant, but no such strong adsorption peak is observed for the ions, also because of the formation of clusters. It should be also be noted that the density profiles appear to be almost symmetric about the central x -plane, which is an indication that the simulation is close to equilibrium. Figure 4 also shows the effect of temperature on the stability of such ionic clusters. As the temperature increases we find the clusters become less stable, and at about 350 K, as shown in Figure 4, the ions

actually start permeating the membrane and are thus observed in the solvent compartment. In addition the peaks in the density profile of ethanol also become less pronounced,

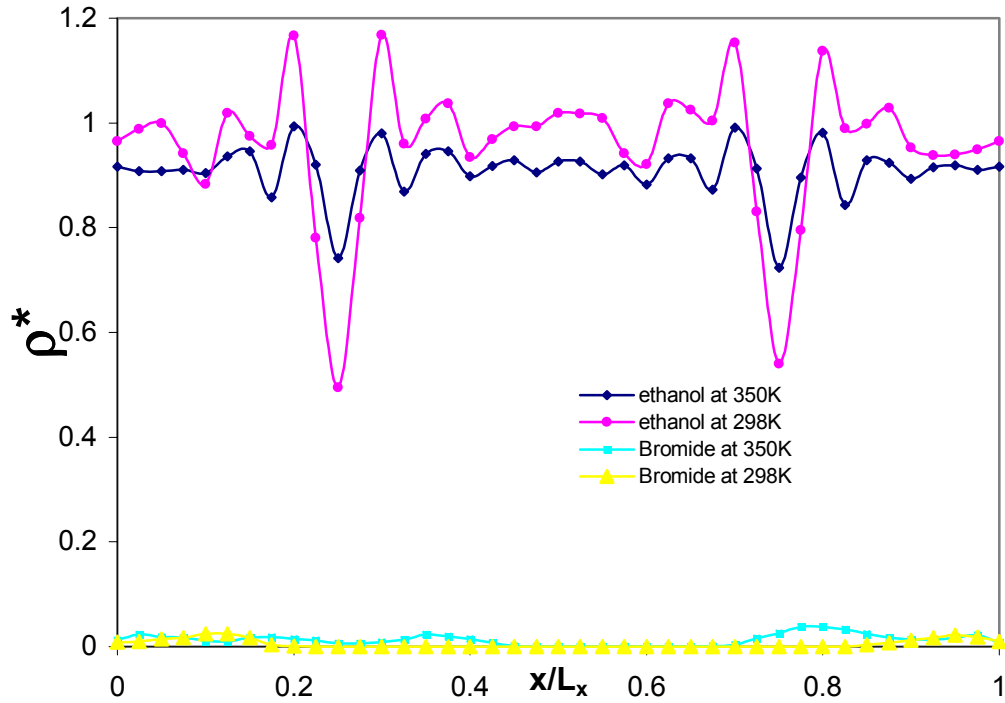


Figure 4: Density profile for a 0.45M NaBr solution at 298 and 350 K.

indicating a decrease in the solution structure as the temperature is increased. This observation has also been confirmed experimentally, where it is well known that at high temperatures the ion rejection rate of membranes decreases dramatically – further confirming the important role ionic clusters play in membrane-based separation processes [23]. We also observed a similar effect on the stability of clusters due to an external electric field, which will be discussed below.

We have also examined the role of an external electric field on separations with semi-permeable membranes, usually referred to as electro-osmosis. Our results show that an external electric field does indeed in most cases speed up the rate of this separation. It is not always clear if at equilibrium the separation is greater, although it does appear to be in some cases. A typical case is shown in Figure 5, where we plot $\langle N_C \rangle$ vs time, $\langle N_C \rangle$, being a running average during the entire simulation of the resultant number of molecules that

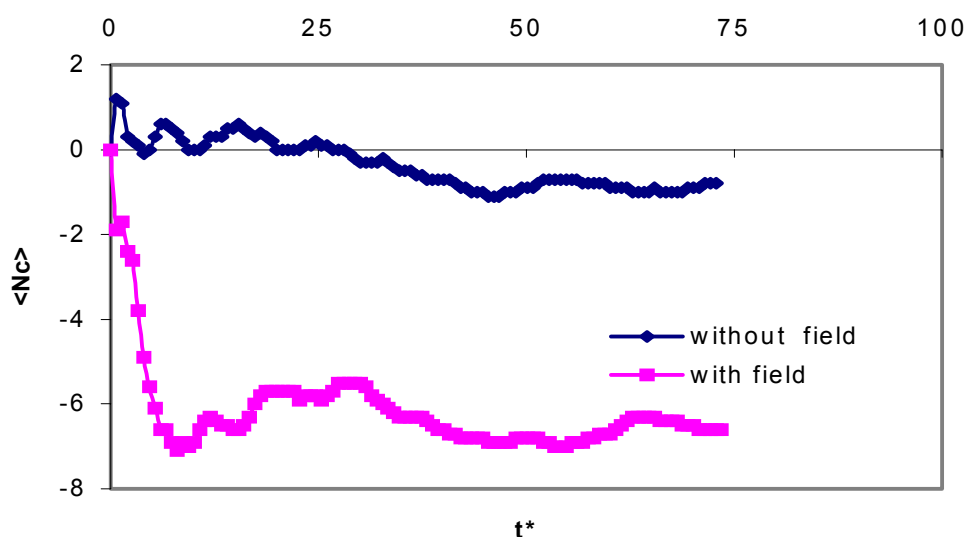


Figure 5. Comparison of average number of solvent crossings for NaBr solutions with and without an external electric field.

have moved across the membrane. The results are for a 0.3 M NaBr solution at a temperature of 25 °C. The figure shows that the system reaches equilibrium faster in the presence of an electric field. In addition it is also clear that the initial rate of reverse osmosis is much larger in the presence of an electric field. We have found this to always be the case, although the final equilibrium state in some cases was not found to be as dramatically different as in this case. That seems to depend upon the concentration of the

electrolytes as well as the strength of the electric field. The results shown are for a reduced alternating electric field (direction switched every 2,500 steps) of unity.

If the strength of this field is increased further we have observed that ions begin to permeate the membrane. This is an effect similar to the temperature effect noted earlier. The electric field makes larger clusters less favorable energetically, and this initially leads to increased reverse osmosis and finally the clusters become so unstable that the ions are also able to break away from these clusters and permeate the membrane. This can be seen from the density profiles shown in figure 6 and the effect of the electric field on the mean-square displacement of ethanol molecules shown in figure 7. Similar results were

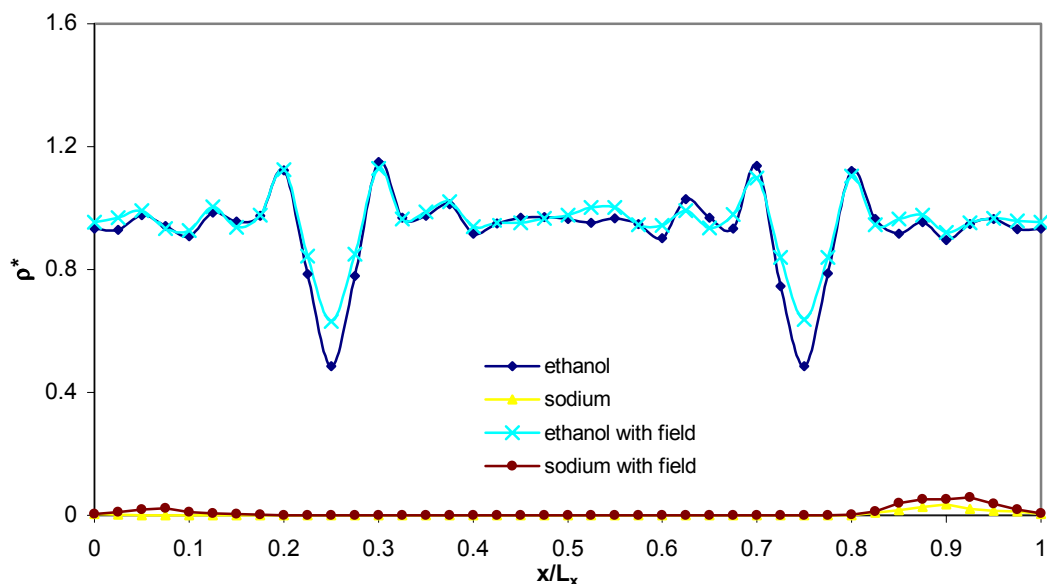


Figure 6: Density profiles for a 0.3M NaBr solution at 298 K, with and without an electric field

obtained for other solutions studied, including aqueous and methanolic solutions [21].

Figure 6 shows that in the presence of an electric field the solution becomes less structured

as evidenced by the less pronounced peaks in the density profiles, especially near the membrane. This makes it easier for the ethanol molecules to break away from the larger clusters and permeate the membrane. This is also confirmed by Figure 7, which shows that the mean-squared displacement of the ethanol molecules (ie their mobility) increases in the presence of the electric field, thus leading to the larger rates of reverse osmosis observed in our simulations. Similar trends have been observed experimentally for electro-osmosis in solutions [24]. In our previous study of polar solutions [5], we found that only the rate of

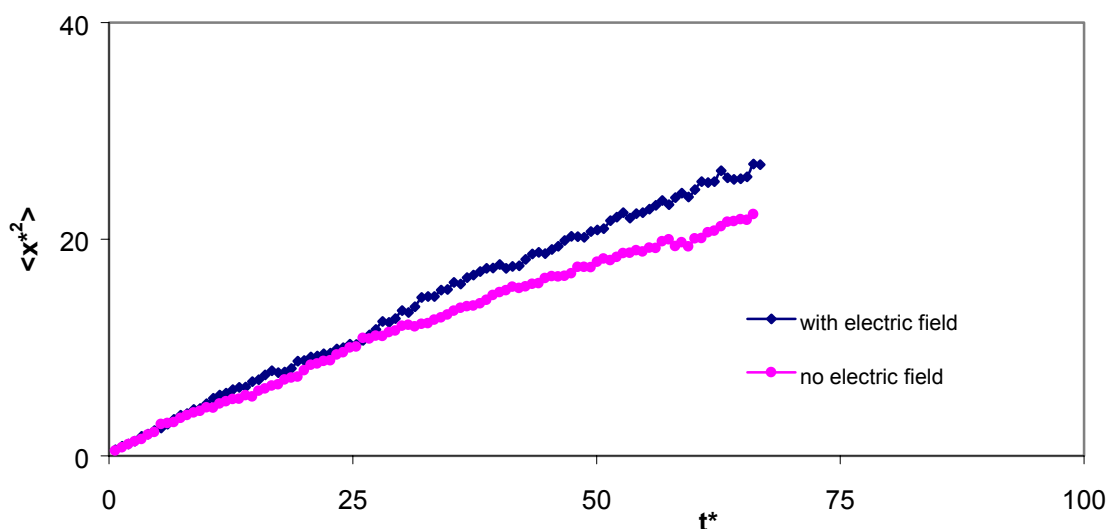


Figure 7: Mean-squared displacement for a 0.3M NaBr solution at 298 K, with and without an electric field.

separation, but not the final separation is affected by the external electric field, which may be quite possible here too for some cases

, based on our results.

CONCLUSIONS

We have reported molecular simulations of osmosis, reverse osmosis and electro-osmosis. Our results have shown that ionic solvations play a significant role in reverse osmosis based separations. In addition we have been able to show that external electric fields can be a useful tool for increasing the rate of reverse osmosis.

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